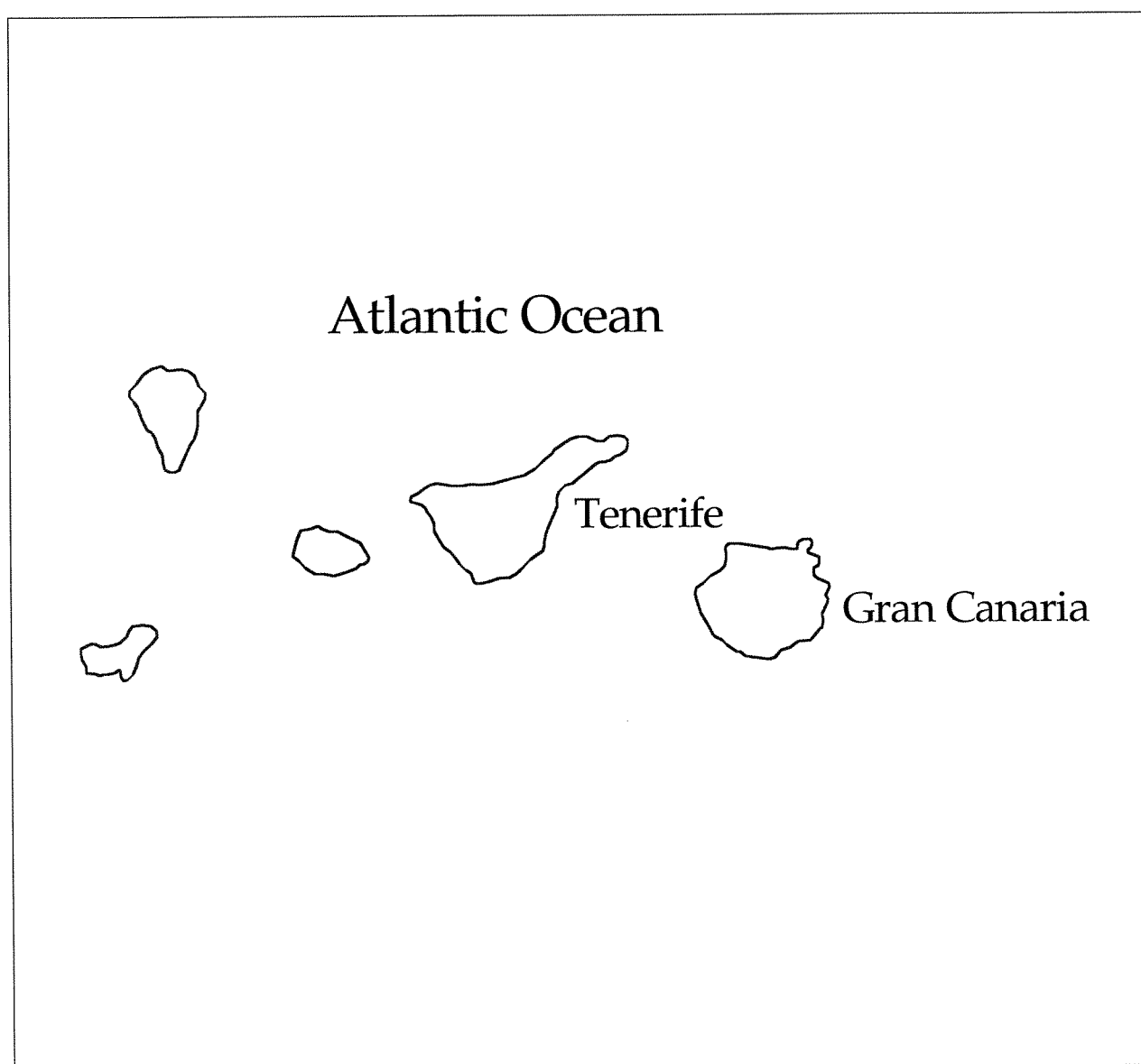


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Analytical Chemistry
intercomparison between
University of La Laguna
(ULL), University of Las
Palmas (ULP), and
Norwegian Institute for
Water Research (NIVA)



Norwegian Institute for Water Research

REPORT

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Abstract

As a part of the evaluation of chemical procedures applied in the baseline survey at two power plant locations at the Canary Islands, an intercomparison was organized between the University of La Laguna (ULL), the University of Las Palmas (ULP), and Norwegian Institute for Water Research (NIVA). The chemical variables analyzed were ammonia, nitrate + nitrite, and heavy metals in sea water, and heavy metals and PAH (polyaromatic hydrocarbons) in sediments and biological materials. One of the sea water samples was a certified reference material, and the others were natural sea water spiked with known amounts of the topical variables. The sediment and the biological material was collected outside the Canary Islands. Varying comparability is in part due to the fact that other methods than agreed upon have been used by the laboratories, and in part that analytical problems have been dominating for the water samples. For heavy metals it is strongly recommended to use the freon extraction method. This method requires that the laboratories must established a lot of experience with the handling technique, and thus are able to control the contamination problems. The comparability between the results for the biological material is acceptable. It is recommended that the laboratories document the analytical quality by the use of certified reference materials, and by participation in the Quasimême intercomparisons.

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Analytical chemistry intercomparison between the University of La Laguna (ULL), the University of Las Palmas (ULP), and Norwegian Institute for Water Research (NIVA). Determination of nutrients and heavy metals in sea water, and metals and PAH in sediment and biological material.

Preface

NIVA has been requested by ABB Environmental, Norway, to evaluate the chemical procedures applied in the baseline surveys at two thermal power plant discharge locations at the Canary Islands. As a part of this evaluation an intercomparison was organized between the University of La Laguna (ULL), Tenerife, the University of Las Palmas (ULP), Gran Canaria, and Norwegian Institute for Water Research (NIVA). A draft report from the intercomparison was written by NIVA, and the participating laboratories were asked to check the informations given, and comment on the conclusions drawn, before the final report was printed.

Oslo, December 15, 1998

Håvard Hovind

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Summary

NIVA has been requested by ABB Environmental, Norway, to evaluate the chemical procedures applied in the baseline surveys at two thermal power plant discharge locations at the Canary Islands. As a part of this evaluation an intercomparison was organized between the University of La Laguna (ULL), Tenerife, the University of Las Palmas (ULP), and Norwegian Institute for Water Research (NIVA). In a meeting in Oslo in the spring 1997 the organization of the intercomparison was agreed upon, and the analytical methods to be used. The central parameters included ammonia, nitrate + nitrite, and heavy metals in sea water, and heavy metals and polyaromatic hydrocarbons (PAH) in sediments and biological materials.

Rather varying correspondence in results between the laboratories was observed for the different chemical variables. The reason for this was partly that different methods had been used, in spite of the methods the laboratories agreed upon to use. Some of the observed differences were also due to technical problems with the analytical method.

For the determination of heavy metals in sea water it was strongly recommended to use the freon extraction method. However, this method is rather difficult to use until the laboratories have established some experience in working with extremely low metal concentrations. Contamination from the laboratory environment and the chemicals used, represent the dominating problems using this method. Typical problem elements are copper, zinc and iron, and the dust in the air may therefore represent a real problem for some of the metals when clean laboratory or laminar flow fume hood is not applied.

The results presented are showing rather clear indications on contamination problems for some of the metals. Here the copper and zinc results from ULL and NIVA are reasonably comparable, except for zinc in one sample. The other metals show rather different results, with deviations between the laboratories of one and two orders of magnitude. The polarographic method seems not to be sensitive enough for these samples.

The results reported for the heavy metals in sediments are generally well comparable, with some few exceptions. The results for the biological sample show acceptable comparability.

The concentration of PAH in the sediments and biological materials collected at the actual locations outside the Canary Islands was very low, and the most sensitive methods have to be used for these samples if significant values should be measured.

It is recommended that the analytical quality is documented by the laboratories by using certified reference materials together with the survey samples, in addition to the participation in the Quasimême intercomparison programme which includes all the analytical variables and samples which are of interest in this project.

1. BACKGROUND

NIVA has been requested by ABB Environmental, Norway, to evaluate the chemical analytical procedures applied in the baseline surveys of the marine recipients outside the thermal power stations at Granadilla, Tenerife, and Barranco de Tirajana, Gran Canaria. Both stations are equipped with Sea Water Flue Gas Desulfurization (SWFGD) units delivered by ABB Environmental. As a first part of this task the procedural principles and limits of detection for the determination of metals and hydrocarbons in sediments and biological materials, in addition to metals and nutrients in sea water, was evaluated. Then it was revealed that the two laboratories differed somewhat in the description of the procedures used for the same parameter in the two surveys. In some cases it was uncertain if this were due to differences in the description only or if the procedures were different.

The general conclusion of this first stage was that the procedural information available in the reports handed over to NIVA in general was not detailed enough for a thorough evaluation of the analytical quality. Results from analysis of certified materials was not presented to demonstrate the analytical quality. Such control analyses are highly recommended to assess the accuracy of the analyses, in addition it is recommended that these determinations are repeated every time such analyses are performed, to document the precision of the analysis over a period of time.

As solid documentation of analytical quality is becoming of increasing importance in environmental monitoring, and since the results from the monitoring will be assessed for compliance with international environmental standards, it was strongly recommended that the laboratories perform analyses of certified reference materials. The results of such analyses should be presented together with the results from the monitoring surveys to document the analytical quality (accuracy and precision). It was also suggested that an intercomparison should be performed on sediments, biological materials and sea water.

2. THE INTERCOMPARISON

In a meeting in October 1996 in Las Palmas it was agreed upon the organization of an intercomparison between the laboratories ULL, ULP and NIVA on some central parameters. These were ammonia, nitrate + nitrite, and heavy metals in sea water, and heavy metals and polyaromatic hydrocarbons (PAH) in sediments and biological materials.

In a meeting between the three laboratories in Oslo in the spring 1997, the analytical methods to be used in the survey and the intercomparison were agreed upon. It was also decided that NIVA should prepare the sea water samples for nutrients and heavy metals, ULP should prepare a natural sediment sample and ULL a biological sample to be used for the determination of heavy metals and PAH. It also was decided that a certified reference material should be included as one of the samples.

3. PREPARATION OF SAMPLES

3.1 Nutrients in sea water samples

The water samples for the nutrient determinations were prepared from natural sea water collected in the Oslofjord, Norway, at a depth of 60 meters, filtered and then spiked with known amounts of sodium nitrate and ammonium chloride solutions. The average background concentration is used for the calculation of the expected concentration to be found in the four samples, see Table 1. The samples were preserved by the addition of 1 ml 4 mol/l sulfuric acid per 100 ml solution, to stabilize the ammonium content.

Table 1. Background concentrations ($\mu\text{g/l}$) in the natural sea water, added and expected concentrations in the samples A - D.

Sample	$\text{NO}_3+\text{NO}_2\text{-N}$	Added	Expected	$\text{NH}_4\text{-N}$	Added	Expected
A	80	50	130	10	50	60
B	80	25	105	10	75	85
C	80	500	580	10	500	510
D	80	750	830	10	750	760

3.2 Metals in sea water samples

The samples E - G were prepared from filtered sea water collected from the Oslofjord, and spiked with known amounts of metal salt solutions with known concentrations. The background concentrations of this water have been shown to be very low, and therefore very small amount of metals were added (see Table 2). Because of the very low concentrations of heavy metals normally found in sea waters, it was recommended to use the freon extraction method with back extraction into nitric acid solution. This technique is used both for the preconcentration of the metals, and to reduce the matrix concentration, which usually causes serious interference effects in atomic absorption and ICP methods. Sample H was a certified reference sea water, NASS - 4, from the National Research Council of Canada. For this sample we have "true" values to which the the results of the laboratories may be compared.

For transport and storage of the metal samples 250 ml pyrex glass bottles were used, The bottles and the screw cap were soaked for one week in in 7 mol/l nitric acid, then rinsed three times with deionized water and capped. This is the normal procedure for cleaning of mercury bottles at NIVA, this time the same bottles were used for the other heavy metals too. Routinely we use special washed polyethylene bottles for the heavy metal samples: the bottles and the screw cap soaked for one week in 6 mol/l hydrochloric acid, rinsed three times with deionized water, soaked for one week in 7 mol/l nitric acid, soaked three times with deionized water, soaked for one week in 0.015 mol/l nitric acid, and finally emptied without drying and capped. Both these bottles and the glass bottles for the mercury samples are stored in a double

set of plastic bags to avoid contamination from the environment. The samples were preserved with 2.5 ml concentrated nitric acid of suprapure quality, produced by subboiling distillation of *pro analysi* quality acid.

Table 2. Typical background concentrations ($\mu\text{g/l}$) of metals in the natural sea water, and added concentrations in the samples E - H (Hg). Certified values for sample H are also given.

Element	Typical background	E	F	G	H
Hg	< 0.01	0.04	0.06	0.200	0.400
Cd	0.03	0	0.03	0.08	0.016
Pb	0.08	0	0.10	0.25	0.013
Cu	0.50	5	0	0.2	0.228
Zn	7	5	0	2	0.115
Fe	-	0	2	5	0.105
Ni	0.3				0.228

3.3 The sediment sample

The sediment sample was taken manually at Barranco de Tirajana, and transported to the laboratory (ULP) in crushed ice. Arriving at the laboratory the sample was passed through a sieve to collect the 2 mm fraction and the 63 μm fraction. After the sieving the material was freeze dried, and divided into three portions of which two were sent to ULP and NIVA. To every laboratory two subsamples were sent, 60 grams stored on a glass bottle for the PAH determination, and 10 grams stored on a polyethylene bottle for the determination of the heavy metals. No certified material of sediment was included in this intercomparison.

3.4 The biological material

About 150 *Diadema antillarum* (sea urchins) were collected manually at C. T. de Granadilla and transported in water to the laboratory (ULL). Immediately after arrival at the laboratory the shell was removed, and so was also the intestine which may contain sand and algae etc. The rest of the biological material was freeze dried, treated in a mortar, and sieved through 250 μm sieve made out of plast material.

The homogenized material was divided into three portions, of which two were sent to ULP and NIVA, and one was kept at ULL. To every laboratory two subsamples were sent, 60 grams stored on a glass bottle for the PAH determination, and 10 grams stored on a polyethylene bottle for the determination of the heavy metals. This material was rather hygroscopic, and should be stored in a desiccator until analysis. No certified material of biota was included in this intercomparison.

3.5 Mailing of samples

The biological material was mailed from ULL at September 24, 1997, and arrived at the two other laboratories within a few days.

The sediment samples were mailed from ULP at October 10, 1997, and arrived at the two other laboratories within a few days.

The water samples were mailed from NIVA at October 9, 1997, but there was some problems with the delivery. The water samples were packed in two boxes to each laboratory, but did not arrive at the laboratories until two - three weeks later. Unfortunately, two bottles (C, E) were destroyed in the box arriving at the laboratory at the University of La Laguna.

4. RESULTS

4.1 Nitrate + nitrite in sea water samples

Table 3. Nitrate + nitrite in sea water, µg/l as N.

Sample A	ULL	ULP	NIVA		Sample B	ULL	ULP	NIVA
Expected	154	141	131		Expected	106	136	101
value 130	159				value 105	99		
	158					118		
Average	157	141	131			108	136	101
Std. dev.	2.6					9.6		
Sample C	ULL	ULP	NIVA		Sample D	ULL	ULP	NIVA
Expected		132	570		Expected	819	158	840
value 580					value 830	824		
						817		
						820		
Average	*	132	570			820	158	840
Std. dev.						2.9		

* The sample was broken before arrival at the laboratory

The results reported by the laboratories are presented in the Tables 3 - 13. Here all the reported results from each laboratory are presented together with the calculated average and the standard deviation (if more than two results are reported by the laboratory).

For this analytical variable ULL and NIVA have reported comparable results for all four samples, which also were comparable to the expected values calculated from the added amounts of nitrate (see also Table 1). The results from ULP also were comparable to ULL and NIVA for the samples A and B, however, the results for the samples C and D were rather low. ULL did not report any result for sample C because the sample was broken when arriving at the laboratory. All three laboratories used an automated photometric method, based on the cadmium reduction of nitrate in a solution buffered to pH = 8.0 - 8.5, diazotization of the nitrite formed and coupling to N-(1-(naphthyl)-ethylenediamine to an azo dye. The absorbance of the solution was measured at 540 nm. ULP reported that they had problems with the cadmium reduction column, their results indicated that the reduction effect may be too low. Some work is now being done to find the explanation of this problem. Revised results from ULP is given in Table 3.

4.2 Ammonium in sea water samples

Table 4. Ammonium in sea water, µg/l as N.

Sample A	ULL	ULP	NIVA		Sample B	ULL	ULP	NIVA
Expected	115	5.6	61		Expected	123	4.07	87
value 60	131	5.9			value 85	122	3.8	
	120					133		
Average	122	5.75	61			126	3.9	87
Std. dev.	8.2					6.1		
Sample C	ULL	ULP	NIVA		Sample D	ULL	ULP	NIVA
Expected		12.9	471		Expected	1383	0.9	770
value 510		10.4			value 760	1545	1.4	
						1419		
Average	*	11.65	471			1449	1	770
Std. dev.		1.8				85.1	0.4	

* The sample was broken before arrival at the laboratory

The reported results for ammonium in the sea water samples are given in Table 4. The results from ULL and NIVA are reasonable comparable, and deviate from the results from ULP, which were very low. The results from NIVA corresponded to the concentrations calculated from the added amounts of ammonium salts to the sea water (see Table 1). An automated version of the indophenol blue method was used by NIVA, while ULL used a manual version of the same method. This method is known to be very sensitive to the pH of the solution during the colour development, and this may be the reason for the differences observed between the results from the two laboratories. Another rather well known problem is the contamination from the laboratory environment, chemicals and laboratory equipment. Too

high results are often observed when no special precautions are taken to avoid the contamination problem.

ULP used another method based on distillation of ammonia to a boric acid solution trap, for this method they normally use 500 ml of sample. In this intercomparison they had to use a smaller volume, as the total volume mailed to the laboratories was 500 ml, and this should be used for the determination of both nitrate and ammonium. For colour development was used the Nessler reagent, and in principle the detection limit of this method should be low enough for these samples. However, by some reasons not being explained so far, the results from this laboratory are too low.

Both ULL and ULP may determine the nutrients in the survey samples. However, the problems with the nitrogen methods (both nitrate + nitrite and ammonium) reported by ULP must be solved, and a documentation demonstrating that the analytical problems are solved is necessary before the nitrogen compounds are determined on a routine basis in the baseline survey samples. It is strongly recommended that a control sample containing a known amount of the nitrogen compounds, preferably a certified reference material, should be run together with the routine samples.

4.3 Metals in the sea water samples

The samples E - G were prepared from sea water collected from the Oslofjord and filtered through 0.45 μm acetate nitrate membrane filter, and then spiked with known amounts of metal salt solutions with concentrations calculated from weighed amounts of stoichiometric compounds. The background concentrations of this water have been shown to be very low (see Table 2), and therefore very small amount of metals were added. For sample H was used a certified reference sea water, NASS - 4, bought from the National Research Council of Canada. For this sample we have certified values against which the the results of the laboratories may be compared.

ULL and NIVA used the freon extraction method with back extraction into nitric acid solution, for the preconcentration of the metals and to reduce the matrix concentration from the major ions in sea water. ULP used a polarographic technique for the determination of the heavy metals - except mercury - in the sea water samples. They used standard addition technique, with a detection limit of 5 - 200 $\mu\text{g/l}$, which is not sensitive enough for the concentrations found in these samples.

Our experience through several years of application of the freon extraction technique has demonstrated that the method is very difficult to handle in the beginning, until one has got enough experience to handle the contamination problem. In a laboratory environment without "clean laboratory" facilities, it is nearly impossible to reduce the contamination to the background level of the analytical method. In a laminar flow fume hood, or in a clean laboratory of high class, it is possible to get down to acceptable levels by long time training of the analyst and neat control of the contamination problem. Typical problem elements are copper, zinc and iron, which we have experienced as a problem at NIVA through several years. NIVA used a laminar flow fume hood to handle such samples. ULL has prepared an area for this kind of work, however, it is not yet working as a clean laboratory. The dust in the

air may therefore represent a real problem for the determination of some of the metals at the moment. ULP did not use a a laminar fume hood.

The results presented in the tables 5 - 10 are showing rather clear indications on contamination problems for some of the metals. The copper and zinc results from ULL and NIVA are more or less comparable, except for zinc in sample H. The other metals show rather different results, with deviations between the laboratories of one and two decades of unit.

4.3.1 Cadmium

The reported results for cadmium in sea water are presented in Table 5. This metal is normally present in sea water very low concentrations. The results from ULL and ULP are too high compared to the concentrations calculated from the added amounts of cadmium, while the results from NIVA are comparable to these values and to the certified value of sample H. Contamination of cadmium from the surroundings at the laboratories of NIVA has been demonstrated not to represent any problem, documented through the blank control of the freon extraction method through several years, while the situation is not documented at the laboratories of ULL and ULP.

Table 5. Cadmium in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	0.93	0.2	0.043		Expected	2.12	0.2	0.055
value 0.03	1.02	0.3			value 0.06		0.2	
		0.2				1.59	0.1	
		0.2					0.1	
Average	0.98	0.23	0.043			1.86	0.15	0.055
Std. dev.	0.06	0.05				0.37	0.06	
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	0.55	0.2	0.090		Expected	< 0.04	0.4	0.015
value 0.08	0.68	0.2			value 0.016	< 0.04	0.3	
		0.1					0.4	
		0.1					0.3	
Average	0.62	0.15	0.090				0.35	0.015
Std. dev.	0.09	0.06					0.06	

The certified value for sample H is 0.016 ± 0.003 µg/l.

4.3.2 Copper

The reported results for copper in sea water are presented in Table 6. The results from ULL and NIVA are comparable, the concentration level is higher than for cadmium and should therefore be easier to determine. Both laboratories reported results being much higher than the expected value for the samples E - G, indicating that the copper concentration in the sea water

used for the preparation of the samples was higher than normal. The result for sample H is only somewhat higher than the certified value. ULP has reported much higher results than the other two laboratories for the samples E and H, while the results were lower for the samples F and G. No clear explanation for these results has been pointed out so far, but the difference may be due to the polarographic technique used. The lack of comparability between the mean value found and the calculated, expected value indicates that contamination may have occurred.

Table 6. Copper in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	4.55	14	5.1		Expected	5.15	1	4.3
value 5.5	5.44	14			value 0.5		1	
		13				5.47	0.9	
		14					1	
Average	5.00	13.8	5.1			5.31	1.0	4.3
Std. dev.	0.63	0.5				0.23	0.1	
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	6.21	2	4.6		Expected	0.07	3.0	0.38
value 0.7	5.96	2			value 0.228		2.7	
		1				0.57	3.0	
		2					2.5	
Average	6.09	1.8	4.6			0.32	2.8	0.38
Std. dev.		0.5				0.35	0.2	

The certified value for sample H is 0.0228 ± 0.011 µg/l.

4.3.3 Lead

The results reported for lead are presented in Table 7, and are demonstrating that this element is difficult to determine in sea water at low levels, the results from the three laboratories are differing very much. Generally NIVA has reported very low results compared to ULL and ULP, however, NIVA has still reported too high result for lead in the certified sample H. At the moment we do not have any good explanation for these observations, however, it is likely to suggest that the high results reported may be due to some problems with contamination from the laboratory environment.

Table 7. Lead in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	34.1	17	0.13		Expected	75.9	12	0.15
value 0.08	41.8	15			value 0.18		11	
		16				70.8	12	
		15					11	
Average	38.0	15.8	0.13			73.4	11.5	0.15
Std. dev.	5.4	1.0				3.6	0.6	
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	19.3	2.0	0.23		Expected	1.69	2.6	0.033
value 0.25	21.3	2.0			value 0.013	1.75	2.0	
		1.0					3.0	
		2.0					2.5	
Average	20.3	1.8	0.23			1.72	2.5	0.033
Std. dev.	1.4	0.5				0.04	0.4	

The certified value for sample H is 0.013 ± 0.005 µg/l.

4.3.4 Iron

Table 8. Iron in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	5.45	9	25		Expected	9.63	5	9.5
value -	6.33	9			value -		4	
		8				9.65	5	
		9					4	
Average	5.89	8.8	25			9.64	4.5	9.5
Std. dev.	0.62	0.5				0.01	0.6	
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	26.9	3	11		Expected	7.98	7.0	< 5
value -	26.3	2			value 0.105		6.0	
		3				5.50	7.0	
		3					7.0	
Average	26.60	2.8	11			6.74	6.8	< 5
Std. dev.		0.5				1.75	0.5	

The certified value for sample H is 0.105 ± 0.016 µg/l.

The results for iron, presented in Table 8, are quite difficult to compare as the differences between the laboratories are varying in all directions. For this metal NIVA did not use the freon extraction technique, but applied the direct determination in graphite furnace atomic absorption. For this metal we have an additional problem to deal with in sea water, because more than 90 percent of the iron, at pH = 8.3, are normally bound in particulate compounds. The initial treatment of the sample before withdrawing a subsample for analysis, may therefore greatly affect the final result.

4.3.5 Zinc

The results reported for zinc are presented in table 9. This metal is representing another typical example of contamination from the laboratory environment. Taking this problem into consideration, there is a certain comparability between the laboratories, even if there are some differences which are varying for the different samples. The contamination is documented as a problem at NIVA by the fact that the control solution, which is a certified material, always gives higher results than the certified value. Application of a clean laboratory environment is the only remedial action to be taken if this problem shall be solved.

Table 9. Zinc in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	7.98	9	11.2		Expected	4.90	2.0	3.55
value 12	8.75	8			value 7		1.0	
		9				5.39	2.5	
		8					2.0	
Average	8.37	8.5	11.2			5.15	1.9	3.55
Std. dev.	0.54	0.6				0.35	0.6	
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	10.7	4.0	7.55		Expected	4.62	16.0	0.29
value 9	10.2	3.5			value 0.115		15.0	
		4.2				10.8	15.5	
		3.8					15.9	
Average	10.5	3.9	7.55			7.71	15.6	0.29
Std. dev.	0.4	0.3				4.37	0.5	

The certified value for sample H is 0.115 ± 0.018 µg/l.

4.3.6 Mercury

The results for mercury reported by the three participating laboratories are presented in Table 10. The results from ULL are higher than the results reported from NIVA, which are comparable to the concentrations calculated from the added amount of mercury to the sample

solutions. ULP has used a cold vapour technique, however, the analytical method has too high detection limit. For these samples a much more sensitive method should have been used. NIVA and ULL used a gold trap technique for the preconcentration of mercury, before the determination by cold vapour atomic absorption in a 15 cm long quartz cell. This method may work well, down to a detection limit of 0.001 µg/l mercury. NIVA used tin chloride as reduction agent, while ULL used sodium borohydride.

Table 10. Mercury in sea water, µg/l.

Sample E	ULL	ULP	NIVA		Sample F	ULL	ULP	NIVA
Expected	0.35	< 1	0.052		Expected	0.48	< 1	0.071
value 0.040		< 1			value 0.060		< 1	
		< 1					< 1	
		< 1					< 1	
Average	0.35		0.052			0.48		0.071
Std. dev.								
Sample G	ULL	ULP	NIVA		Sample H	ULL	ULP	NIVA
Expected	0.49	< 1	0.202		Expected	0.59	< 1	0.39
value 0.200		< 1			value 0.400		< 1	
		< 1					< 1	
		< 1					< 1	
Average	0.49	< 1	0.202			0.59	< 1	0.39
Std. dev.								

There has been added 0.400 µg/l mercury(II) to sample H.

4.4 Metals in sediment sample

The reported results, given in Table 11, show somewhat varying comparability for the different elements in the sediment sample. Here the digestion method is of major importance, as the acid mixture used affects the temperature during the digestion, and therefore the extraction effect of the different metals. All three laboratories digested the sample with a mixture of hydrofluoric acid and aqua regia, which was the method recommended at the meeting in Oslo in 1997. The mixture of hydrofluoric acid and aqua regia is recommended for the total digestion, as nitric acid alone is known not to extract all the elements bound in the silicate lattice.

Table 11. Metals, µg/g in sediment.

Sediment	ULL 1	ULL 2	ULL 3	Std.dev.	ULL	ULP	NIVA
Cd	0.18	0.21	0.18	0.02	0.19	< 0.5	0.28

Cu	34.0	33.4	33.7	0.3	33.7	25.0	31.1
Pb	45.4	46.0	37.0	5.0	42.8	76.0	82.0
Hg	1.31	1.37	1.31	0.03	1.33	1.5	1.34
Zn	157.9	152.3	160.0	4.0	156.7	123.0	161
Ni	104.1	100.4	106.1	2.9	103.5	74.0	76.8
V	270.0	251.5	268.4	10.3	263.3	114.0	
Fe, mg/g	72.4	70	69.3	1.6	70.6	34.1	70.6

Acceptable comparability is observed for cadmium and mercury, although ULP has too high detection limit for cadmium. For copper and zinc the results are comparable at all three laboratories. For lead ULP and NIVA has acceptable comparability between the results, being about twice as high value as reported from ULL. For nickel ULL has reported somewhat higher result than the two other laboratories, and for iron ULL and NIVA have got the same result, while the result from ULP is about the half value.

To document the analytical quality a certified reference material should be analyzed, and the results reported together with the survey samples.

4.5 Metals in the biological sample

The reported results for heavy metals in the *Diadema antillarum* sample are presented in Table 12. For this kind of sample the results are far more comparable than for any of the other samples of this intercomparison, for most of the cases they may be classified as acceptable. ULL and ULP digested the sample with nitric acid and hydrogenperoxide in microwave oven. NIVA digested the samples by nitric acid alone in a micro wave oven for 30 minutes.

Table 12. Metals, µg/g in biological material.

Organism	ULL 1	ULL 2	ULL 3	Std.dev.	ULL	ULP	NIVA
Cd	7.56	7.85	7.70	0.15	7.70	7.05	6.91
Cu	5.29	5.81	5.18	0.34	5.43	5.4	4.4
Pb	0.41	0.46	0.34	0.06	0.40	0.85	0.7
Hg	0.09	0.16	0.16	0.04	0.14	0.24	0.22
Zn	522.2	526.4	540.3	9.5	529.6	549.0	570
Ni	0.39	0.44	0.32	0.06	0.38	3.9	
V	15.6	16.1	15.5	0.3	15.7	< 25	
Fe	1990	1900	1940	45	1943	1190	2100

4.6 Polyaromatic hydrocarbons (PAH)

The results reported by the laboratories are presented in the Table 13 for the sediment and the biological material, respectively. ULP did not report results for PAH because the instrument was broken at the time when the samples should be analyzed.

Table 13. PAH, µg/kg	Sediment			Organism	
Variable	Laguna	NIVA		Laguna	NIVA
Naphthalene	< 6	1.3		< 13	9.9
2-M-Naphthalene		0.6			4.8
1-M-Naphthalene		0.5			3.5
Biphenyl		<0.5			< 0.5
2,6-Dimethylnaphthalene		<0.5			1
Acenaphthylene	< 7	<0.5		< 13	0.9
Acenaphtene	< 7	0.8		< 14	3.8
2,3,5-Trimethylnaphthalene		<0.5			1
Fluoren	< 6	<0.5		< 12	1.8
Phenantrene	< 5	1.9		1587 ?	4.8
Anthracene	< 6	0.7		< 12	2.1
1- Methylphenantrene		<0.5			
Fluoranthene	< 3	<0.5		< 7	21
Pyrene	< 4	<0.5		< 8	16
Benz(a)anthracene	< 4	<0.5		< 9	2.4
Chrysene / Triphenylene	< 4 (1)	<0.5		< 9	3.3
Benzo(b)fluoranthene	< 16	<0.5		< 33	2.4
Benzo(j,k)fluoranthene	< 16 (2)	<0.5		< 31	2.1
Benzo(e)pyrene		<0.5			masked
Benzo(a)pyrene	< 10	<0.5		< 21	2.7
Perylene		<0.5			0.5
Indene(1,2,3cd)pyrene	< 31 (3)	<0.5		< 63	2.4
Dibenzo(a,h)anthracene		<0.5			<0.5
Benzo(ghi)perylene	< 8	<0.5		< 15	1.4
Sum PAH		5.8			87.8

- 1) Chrysene only
- 2) The k isomere only
- 3) Coelution with dibenzo(a,h)anthracene

The methods used by ULL and NIVA are based on the same principles, however different in some respects, and it should therefore be expected some differences in the results. The laboratories are extracting the sediments with cyclo-hexane, determining the PAH by gas chromatography with flame ionization detector. However, there was some problems with the separation of the two liquid phases. NIVA is using dimethylformamide in the cleaning step. The detection limits of the method used at ULL are too high for the samples analyzed here. The concentration level demands the detection level to be lowered to one tenth of the level used here.

NIVA adds the internal standards to the samples and then extracts the PAH compounds with dichlormethane in soxhlet apparatus. The extract is cleaned through a GPC processes to remove disturbing compounds. At the end of the process the extract is analyzed by GC/MSD. The PAH compounds are identified with MSD by the retention times and the molekül ions of

the compounds. The quantification is performed with the internal standards. Biological materials are added the internal standards and saponified before extraction with n-heptan. The extract is cleaned with GPC and determined with GC/MSD.

The results seems to be comparable, however, the method used by ULL has higher detection limit than the method used by NIVA, and therefore ULL has mainly reported results as “less than”. The PAH concentrations in both the sediment sample and the biological material were very low.

5. Discussion

The nutrients may be determined at the university laboratories. However, the problems with the nitrogen methods (both nitrate + nitrite and ammonium) reported by ULP must be solved, and a documentation demonstrating that the analytical problems are solved is necessary before the nitrogen compounds are determined on a routine basis in the baseline survey samples. It is strongly recommended that the laboratories participate in the Quasimeme intercomparisons run by ICES In addition, a control sample containing known amount of the nitrogen compounds, preferably a certified reference material, should be run together with the routine samples.

The differences between the results reported for heavy metals in sea water were unacceptably large. Normally we use glass bottles for mercury samples and plastic bottles for the other heavy metals in sea water samples. This time we used the same glass bottles for all the heavy metals. However, there is no reason to believe that the glass bottles would affect the results produced at the laboratories. If there were a contamination effect caused by the bottles used, this should have been demonstrated through higher results from NIVA too. The generally higher results produced by ULL and ULP compared to NIVA, indicate that the differences are caused by other problems, most probably by contamination from the laboratory environment.

Because of the low concentration levels of heavy metals in sea water samples, it is absolutely necessary to apply the freon extraction method, or another method with equivalent sensitivity, for this kind of samples. The differences in the results from the three laboratories demonstrate that the freon extraction method is difficult to handle, and it is recommended to use a clean laboratory, or a laminar flow fume hood, for the treatment of the sample to reduce the problems with contamination from the laboratory environment. It is recommended to use certified seawater as a control sample to document the quality of the analytical method. It is a problem that the polarographic method used by ULP is not sensitive enough to determine heavy metals in the sea water samples.

For the determination of the heavy metals in sea water it is very important to focus on the contamination problem during sampling at the sea. To avoid, or more correctly, to reduce the contamination in this process, it is higly recommended to use Go-Flo sampler, which in advance have been washed according to a special procedure. This kind of sampler (General Oceanics Inc.) are all plastic construction and are opened after it has been lowered beneath the water surface. If there is no earlier experience in using this kind of sampler at ULL and ULP, it is recommended that NIVA participate in the first sampling where sea water samples are collected, so that personal at these laboratories may learn the special technique used.

The comparability of the results for heavy metals in sediment and biological material reported by the three laboratories are acceptable. It is recommended that the sediments are digested in hydrofluoric acid and aqua regia to give the total content of the metals in the samples. These results would then be comparable to the data in the ICES international data base. To document the analytical quality a certified reference material should be analyzed and the results reported together with the samples of the survey samples.

For the determination of PAH the results from this intercomparison demonstrate that a more sensitive method has to be used for the low concentration samples that are collected at the actual locations. It is necessary to reduce the determination limit to about one tenth of the limit used by ULL in the reported results. A close, direct cooperation between the analysts at NIVA and ULL will probably solve this problem. The use of a certified reference material should be included in the series of samples, both for sediments and biological materials, and the results of these materials should be reported together with the results of the survey samples.

It is generally recommended that the laboratories participate in the Quasimême intercomparison run twice a year. In these intercomparisons are included the determination of nutrients in sea water samples, and metals and PAH in both marine sediments and biological materials of different kind. These intercomparisons are organized by The Scottish Office, Marine Laboratory, P.O.Box 101, Victoria Road, Aberdeen, Scotland.